Preparation and characterisation of thermomechanical properties of sol-gel derived glasses in the PbO-SiO_2-B_2O_3-ZnO system

M. Mennig, A. Kalleder, H. Schmidt
Institut für Neue Materialien, Universität des Saarlandes
Im Stadtwald, D-66 123 Saarbrücken

1 Introduction

Silicate glasses with high contents of lead oxide are for example used as optical glasses and as solder glasses. In spite of the numerous usabilities [1,2] their manufacturing is sometimes difficult, since these melts are chemically aggressive, and the evaporation of lead during melting cannot be avoided. The sol-gel process may be assumed to be an alternative preparation route [3,,5], since lower temperatures can be used and more homogeneous glasses can be obtained. Thus mixing problems of SiO_2 and PbO due to very different densities could be avoided.

A sol-gel synthesis route to SiO_2-PbO-B_2O_3 coatings on glass is described by James and Strtawbridge [6,7], where the PbO content is limited to 30 mole% probably by phase separation. Yamane describes the preparation of glasses in the same system with a maximum PbO content of 24 mole% [8] using lead acetate and lead nitrate as precursors for Pb, tetraethoxysilane as a precursor for Si and boric acid as boron oxide precursor. Xerogels could be densified to glasses during thermal treatment at first in oxygen and then in helium atmosphere after 60 h and a temperature of up to 600 °C.

A new synthesis route to organic free binary PbO-SiO_2 xerogels with PbO contents up to 70 mole% was found recently [9], that could be melted to homogenous glasses in air at temperatures between 725 °C and 975 °C.

The aim of this paper was to develop a sol-gel synthesis for ternary and quaternary glasses in the PbO-SiO_2-B_2O_3(-ZnO) system for obtaining low processing tempera-trues. Glasses with PbO-contents of about 50-70 mole% were investigated due to their technical relevance, e.g. for solding or glazing.

2 Experimental

Sols were synthesised from lead nitrate, tetraethoxysilane (TEOS), trimethylborate

and zinc acetate dihydrate in water solution using 0,1 M nitric acid as catalyst. Gels were obtained after stirring at 60 °C for 6 h and dried to xerogel powders at 120 °C for 12 h. After thermal removal of residual nitrates at temperatures between 470 °C and 485 °C for two hours the xerogel powders were melted at temperatures between 650 °C and 715 °C depending on the glass composition (compare table 1). The melts were poured in a preheated graphite mould and annealed according to DIN standards [10]. The batch composition and the sample markings are given in table 1.

Table 1: Composition (synthesis) of the different prepared glass samples

oxide content		sample							
		P78	P78B10	P78B10Z	P83B6.6	P83B13	P83B13Z	P89	P89B5.2
PbO	/wt.%	78,8	78,8	78,8	83,0	83,0	83,0	89,6	89,6
	/mole%	50,0	51,7	52,1	58,1	59,5	60,2	70,0	71,3
SiO_2	/wt.%	21,2	11,2	10,0	10,4	4,0	2,4	10,4	5,2
	/mole%	50,0	27,3	24,5	27,1	10,6	6,4	30,0	15,4
B_2O_3	/wt.%	-	10,0	10,0	6,6	13,0	13,0	-	5,2
	/mole%	-	21,0	21,2	14,8	29,9	30,2	-	13,3
ZnO	/wt.%	-	-	1,2	-	-	1,6	-	-
	/mole%	-	-	2,2	-	-	3,2	-	-

The binary samples P78 and P89 were prepared as described in [9], using basic lead acetate and tetraethoxysilane (TEOS) as precursors, dissolved in a mixture of acetic acid of 10 % and ethanol with 1 M nitric acid as catalyst. The PbO-content of the glasses was 66,7 , 78,8 and 89,6 wt.% by batch (65,8 , 79,2 and 89,4 wt.% by analysis). Their properties are used for a comparison to the ternary and quaternary glasses.

Thermal analysis was carried out using a Bähr DTA/TG Typ 501 measuring in Al_2O_3 crucibles at synthetic air. Thermomechanical analysis (TMA) was carried out with a Bähr T.M.A. 2000 using glass beams of 10 mm in length and 5 mm in height and width and a heating rate of 5 K / min. Viscosity was investigated using a Bähr Viskosimeter Typ 401. The samples for the beam bending experiments were 5 mm in length, 3 mm in height and 5 mm in width.

3 RESULTS AND DISCUSSION

3.1 Preparation of xerogels and glasses

Investigations to transfer the experimental route developed in [9] to the four component system lead to problems to remove organics. Using trimethylborate (TMB) as precursor for B_2O_3 and zinc acetate dihydrate as a precursor for ZnO with nitric acid to catalyse hydrolysis and condensation, gels could be obtained after stirring for 3 h at 50 °C and the appropriate xerogels could be prepared during drying at 120 °C. But it was not possible to prepare glasses by thermal treatment, because the xerogels still contained acetic groups. In the case of the binary system they could be removed at temperatures around 275 °C because of the porosity of the xerogel powders at this temperature. In the ternary and quaternary systems only black coulored agglomerates but no homogenous glasses were obtained even after thermal treatment in oxygen atmosphere, using very small heating rates (0,5 K/min) and temperatures up to 800 °C. It is assumed that due to the lower T_g or a different microstructure of the B_2O_3 containing systems the xerogel is densified during thermal treatment before the acetates are burned off.

In order to overcome this problem the substitution of lead acetate by $Pb(NO_3)_2$ was investigated since it decomposes at temperatures around 470 °C. In fig. 1 the flow chart of the newly developed synthesis route is shown. The chart represents an optimized procedure, where concentrations of precursors and temperatures had been varied systematically. It has to be mentioned, that the sol-gel synthesis takes place in a water based, almost organic free solvent system.

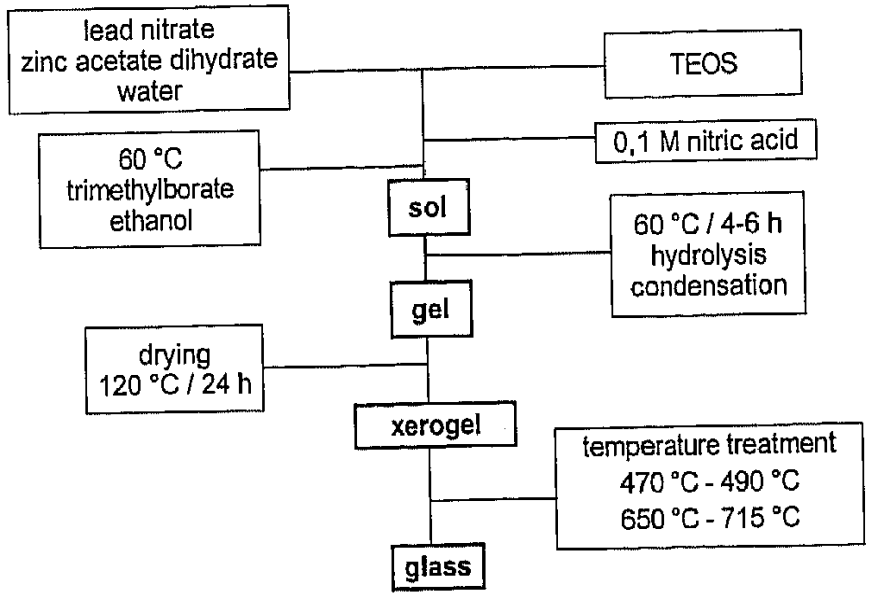

Fig. 1 : Scheme of the developed sol-gel process

After mixing the precursors for Pb, Zn and Si and dropwise addition of trimethylborate liquid and slightly cloudy gels were formed by hydrolysis and condensation at 60 °C. The gelation time increased with decreasing TEOS amount from 6 h to 4 h. Fine, white xerogel powders with particles of about 10 µm in size and homogenous composition could be prepared by rapid drying at 120 °C and without milling, as indicated by FEG-SEM investigation in combination with EDX-analysis.

Fig. 2 shows the result of the thermal analysis of the three component xerogel powder of a glass with 83,0 wt.% PbO, 13,0 wt.% B_2O_3 and 4,0 wt.% SiO_2, (P83B13 in tab. 1) and of pure $Pb(NO_3)_2$.

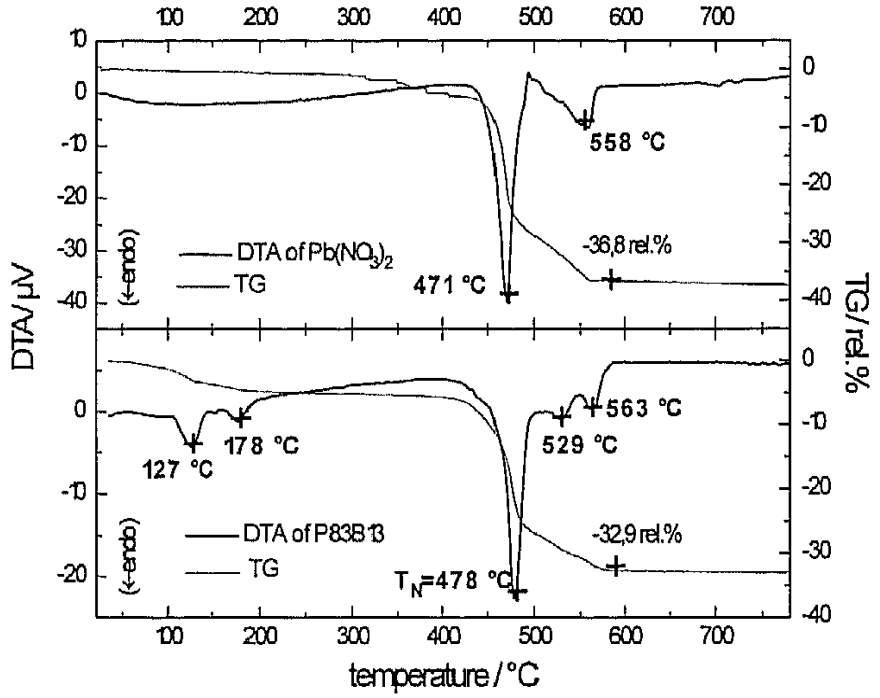

Fig. 2: Thermal analysis of the P83B13 system xerogel and of pure lead nitrate in synthetic air using a heating rate of 10 K/min

The slight weight loss between 20 °C and 200 °C is caused by the removal of water out of the gels dried at 120 °C and of ethoxide groups from TEOS. This slight weight loss increases with increasing amounts of TEOS. The large peak at 478 °C (T_N see fig. 2) represents the decomposition of lead nitrate, which can be seen comparing the DTA curve of pure $Pb(NO_3)_2$ in fig. 2. It is assumed that the peak at 529 °C is due to the decomposition of residual $-CH_3$ or $-OCH_3$ groups from trimethylborate. The peak at 563 °C is assumed to be a phase transformation of PbO, since it also occours with pure $Pb(NO_3)_2$.

Fig. 2 also shows a total weight loss of about 32,9 rel.% at a temperature of about 580 °C. This is in very good agreement with the estimated weight loss from the total

temperatures varied in dependence on the compostion, e.g. T_N between 470 °C and 490 °C. The detected weight loss increases with increasing PbO content of the glasses to be prepared between 29,2 rel.% (sample P78V10) and 33,2 rel.% (P89B5.2),

Temperature treatment of the xerogel powders in the decomposition range of lead nitrate between 470 °C and 490 °C for 4 h in air results in clear and compact, completely degassed glasses. This temperatures are remarkable lower than the melt temperateures of appropriate glas melts between 1100 °C and 700 °C [11], containing 71,3 wt.% to 85,0 wt.% lead oxide.

AAS and ICP measurements showed that the glass compositions are in good agreement to the batch compositions within the errors of measurement. All glasses were X-ray amorphous. To get a comparison between sol-gel derived and melted glasses some of the thermomechanical properties of thus prepared glasses are described in the following.

3.2 Thermal coefficient of expansion and the transition temperature

Using TMA thermal expansion between 20 °C and 300 °C ($\alpha_{20\text{-}300}$) and transition temperature (T_g) were studied. Table 2 shows the measured data including the data of binary lead silicate glasses [9] and data of melted glasses [12].

Table 2: Thermal coefficients of expansion ($\alpha_{20\text{-}300}$) and transition temperatures (T_g) of the prepared glasses determined by TMA including data of melted glasses from [12]

sample	T_g / °C	$\alpha_{20\text{-}300}$ / 10^{-6} K^{-1}	calculated values [12] $\alpha_{20\text{-}300}$ / 10^{-6} K^{-1}
P78	414	8,73	8,90
P78B10	366	10,51	-
P78B10Z	361	9,84	-
83,0PbO-17,0SiO_2	-	-	9,83
P83B6.6	321	11,21	-
P83B13	317	11,49	-
P83B13Z	313	11,00	-
P89	347	11,29	11,66
P89B5.2	294	12,02	-

The thermal coefficient of expansion (TCE) of the glass P89B5.2 was determined in the range between 20 °C and 280 °C, because of the remarkable low T_g of 294 °C.

The transition temperature of a melted glass with the same composition is not described in literature. Merker et al. [12] found for lead silicate glasses with PbO-contents of 78,8 wt.% (analogous to sample P78) and 88,2 wt.% (50,0 and 66,7 mole%) T_g's of 410 °C and 349 °C, which are comparable to the data for sol-gel derived binary glasses.

For calculating $\alpha_{20\text{-}300}$ of melted lead silicate glasses with PbO-contents between 50 mole% and 66,7 mole% using the formula

$$\alpha = \sum_i \alpha_i p_i \quad , \qquad \{1\}$$

where p_i is the content of each oxide in mole percent and α_i is the corresponding coefficient, Merker et al. [12] determined α_{PbO} to be 1,58 and α_{SiO_2} to be 0,20. Using these coefficients $\alpha_{20\text{-}300}$ for some melted binary glasses were calculated (compare table 2).

It can be seen that the measured thermal coefficients of expansion of sol-gel glasses concord to the calculated values. Comparing $\alpha_{20\text{-}300}$ of the binary PbO-SiO_2 glass P83 and of the prepared lead borosilicates of the P83-series, the known influences of B_2O_3 are evident.

3.3 Viscosity measurements

To prepare samples with geometry's needed for further investigations like beam bending viscosimetry and dilatometry, the glass melts were heated up further to temperatures which allowed pouring in a preheated graphite mould. These temperatures varied between 650 °C and 715 °C according to the glass composition. The melts were free of gas bubbles since all gaseous products had been eliminated at temperatures between 470 °C and 490 °C. After annealing compact, transparent and intensively yellow coloured glasses could be obtained.

With beam bending viscosimetry the viscosity-temperature characteristic of the prepared glass was studied. The following figure shows the η/T-curves of the samples P83B6.6, P83B13, P83B13Z, P89 and P89B5.2 including two curves of melted galsses [13] with the compositions 82,0PbO-18,0SiO_2 and 84,7PbO-15,3SiO_2..

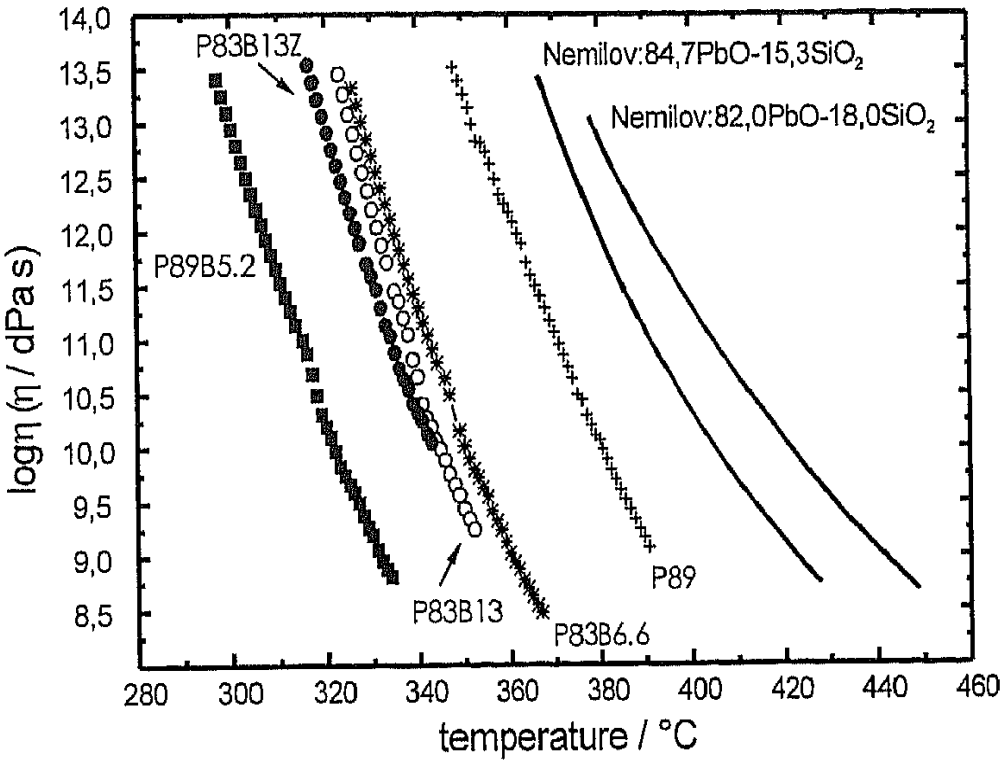

Fig. 3: Viscosity versus temperature curves from beam bending measurements of sol-gel derived glasses compared with some obtained by melting [13]

Comparing the curves from the samples P89 and P89B the strong viscosity decreasing influence of the substitution of SiO_2 with boron oxide can be seen. The same effect could be regarded while comparing sample P83B6.6 and the curves of melted glasses [13] with PbO-contents of 84,7 wt.% and 82,0 wt.%. Due to a further substitution of SiO_2 the differences are getting smaller. The η/T-curves of the P83-series also show the influence of zinc oxide, which causes longer glasses. This effect was also detected in the glasses of the P78-series, not represented in fig. 3.

A comparible effect of B_2O_3-addition to alkali silicate glasses is well known [14]. Glass properties, like viscosity, show a minimum or maximum with increasing B_2O_3-content, that is explained with a change of the coordination number of the boron atom between $[BO_3]$ and $[BO_4]$. For high lead containing glasses such effects are not described in literature yet, so this has to be investigated more in detail.

4 Conclusion

The sol-gel process is suitable to prepare homogenous glasses in the PbO-SiO_2-B_2O_3-ZnO system with PbO contents up to 71,3 mole% (89,6 wt.%). It has to be emphasized that the developed synthesis route takes place in an almost organic free, water based solvent system. The investigation has shown that those prepared glasses can be obtained by melting of appropriate xerogel powders in air. The

thermomechanical properties of the obtained glasses are in a good agreement with those of melted glasses.

The preparation of appropriate glasses by high viscous sintering at temperatures around T_g seems possible if two conditions could be fullfilled. A synthesis route has to be found, where all residual organic and inorganic groups can be removed from xerogels at temperatures bellow the T_g of the corresponding glass and a processing route has to be developed, leading to xerogel powders of suitable particle size distribution.

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